Seeking Heteroatom-Rich Compounds: Synthetic and Mechanistic Studies into Iron Catalyzed Dehydrocoupling of Silanes

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Abstract

A detailed synthetic investigation into the dehydrocoupling of silanes with amines, phosphines and alcohols using an iron pre-catalyst (**1**) is presented. We have furnished over 30 examples of aminosilane synthesis along with kinetic studies using MeBnNH and $MePhSiH_2$ as coupling partners. The kinetic studies suggest a reversible reaction with silane which generates aminosilane and an Fe-hydride dimer that undergoes rate-limiting protonolysis with amine with N–H bond cleavage in the transition state, consistent with a primary KIE of 2.42(3). The presence of dimers as on-cycle intermediates were analyzed in depth. Beyond this we have explored substrate scope of phosphinosilane formation which shows a preferential heterodehydrocoupling to give the phosphinosilane with primary and secondary silanes. Silylethers can also be prepared and alcohols that contain alkene functionality do not show any tendency to reduce the double bond.

Keywords

Dehydrocoupling, homogeneous catalysis, reaction mechanisms, iron, silanes

Introduction

Dehydrocoupling of p-block compounds is an attractive method with which to generate hydrogen gas. There has been a great deal of focus in the literature, using a wide range of metal pre-catalysts, on heterodehydrocoupling of amine-boranes, most notably ammonia-borane ($H_3N{\cdot}BH_3$) because of the high weight% of H_2 that can be released from this simple molecule.[1] Although there has been focus on dehydropolymerization of amine- and phosphine-boranes for the preparation of materials with novel properties, there are limited examples of dehydrocoupling and dehydropolymerization of silanes with protic substrates such as amines, phosphines and alcohols.

Much of the seminal research into homogeneous catalysis for amino- and phosphinosilane formation via dehydrocoupling was carried out by Harrod,[2] covering several elegant examples using titanocene catalysts,[3, 4] and by Eisen using uranium amides for N–Si bond formation.[5] Other examples of aminosilane formation by dehydrocoupling include work from Hill,[6, 7] Sarazin[8-11] and Nembenna[12] on Group II catalysis, Crimmin[13] and Guan using Ca[14] and Y,[15] Sadow exploring Mg[16] and a range of lanthanides,[17] Tsuchimoto with Zn[18] and Wright using Al.[19] In general, catalytic aminosilane formation is facile, with most examples in the literature being performed at room temperature in a few hours, with the exception of particularly sterically hindered reagents, which often need heating. In contrast the formation of phosphinosilanes tends to require more forcing conditions and there are far fewer examples in the literature. Recent work from Manners has demonstrated that tris(pentafluorophenyl)borane (BCF) can be used in conjunction with tertiary silanes at 100-130 °C to prepare phosphinosilanes along with elegant examples of cyclic

phosphinosilanes when a primary or secondary silane is employed.[20] Waterman has used $La[N(SiMe_3)_2]_3$[21] and a Zr catalyst for heterodehydrocoupling[22] along with silylene elimination from silazanes[23] and Stephan has undertaken P–P bond activation to furnish phosphinosilanes using a Rh catalyst.[20, 24] There are few examples of transition metal catalyzed dehydrocoupling methods for silylether formation, with examples in the literature being limited to late transition metals (likely due to oxophilicity in the early to mid-transition metals). Ito and Sawamura have reported using Cu[25] and Au[26, 27] while Yamada has tested a range of acetylacetonate (acac) salts, with $Cu(acac)_2$ giving the highest yields (important to note is the very low reactivity obtained with $Fe(acac)_2$).[28] Sadow has developed a Zn system[29] and Grubbs has reported an attractive NaOH catalyzed method,[30] but most examples are transition metal-free and follow on from Piers' early report of high levels of reactivity using tertiary silanes and a range of alcohols in the presence of BCF catalyst.[31-33]

We saw iron catalyzed heterodehydrocoupling as a remarkably simple route to prepare highly functionalized silane-protected molecules that have a range of applications. In terms of small molecule chemistry, aminosilanes have been used as masked ammonia reagents in Pd-catalyzed aryl-N bond formation, and undergo facile deprotection to reveal the desilylated aniline product[34] and are postulated intermediates in catalytic Staudinger amidation reactions.[35] Phosphinosilanes have been used in Pd-catalyzed cross-coupling by Stille to prepare tertiary phosphines,[36] by Clarke[37] and Yang and Sun[38, 39] in Ni-catalyzed cross-coupling and for C–CN bond activation. Gudat undertook an organocatalytic approach in cross-coupling to prepare P–C bonds from dihalide reagents and $TMS–PPh_2$.[40] More recently phosphinosilanes have been used by Hirano and Miura for the preparation of 1,2-diphosphines[41, 42] and by Daugulis to functionalize benzynes,

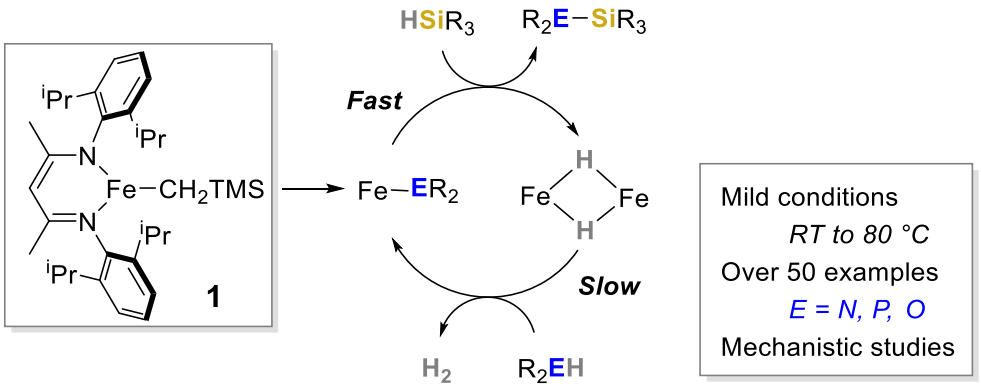
utilizing both Si and P components of the reagent.[43] Oro has also used both components of the phosphinosilane for the Ir-catalyzed functionalization of CO_2.[44]

Silylethers are ubiquitous in protecting group and traceless directing group[45] strategies in organic synthesis. R_2HSi-protected alcohols can be easily deprotected using standard acidic work-up procedures as demonstrated by Brunner,[46] Nile[47] and Lavastre and Morken.[48] Hartwig used dehydrocoupling to prepare silylethers using an Ir catalyst and the silylether product was then used as a directing group in C–H borylation,[49] Tamao-Fleming oxidation or Hiyama coupling of benzoxasiloles,[50] which is also formed using an Ir catalyst. Herzon has also recently reported elegant studies into C–H functionalization of (+)-Pleuromutilin[51] where the resulting tertiary siloxane was used to undertake an iridium catalyzed C–H bond silylation and subsequent Tamao-Fleming oxidation of the silylated carbon.

Beyond the heterodehydrocoupling of silanes to prepare silyl-protected organic motifs, polysilazanes are used as coatings and precursors to ceramics[52, 53] while polysiloxanes (or silicones) are widely used materials with applications that include elastomers, lubricants, foams and adhesives.[54, 55]

The chemistry that has already been developed using the iron(II) pre-catalyst **1** demonstrates the versatility of this complex, particularly in main group bond transformations that appear to be redox neutral at iron.[56-62] However, we are continually seeking to understand the fundamental bond making and breaking processes involved in catalysis with this complex in order to try to develop new modes of reactivity. We herein present our synthetic and mechanistic investigations into dehydrocoupling and dehydropolymerization to prepare aminosilanes, phosphinosilanes and

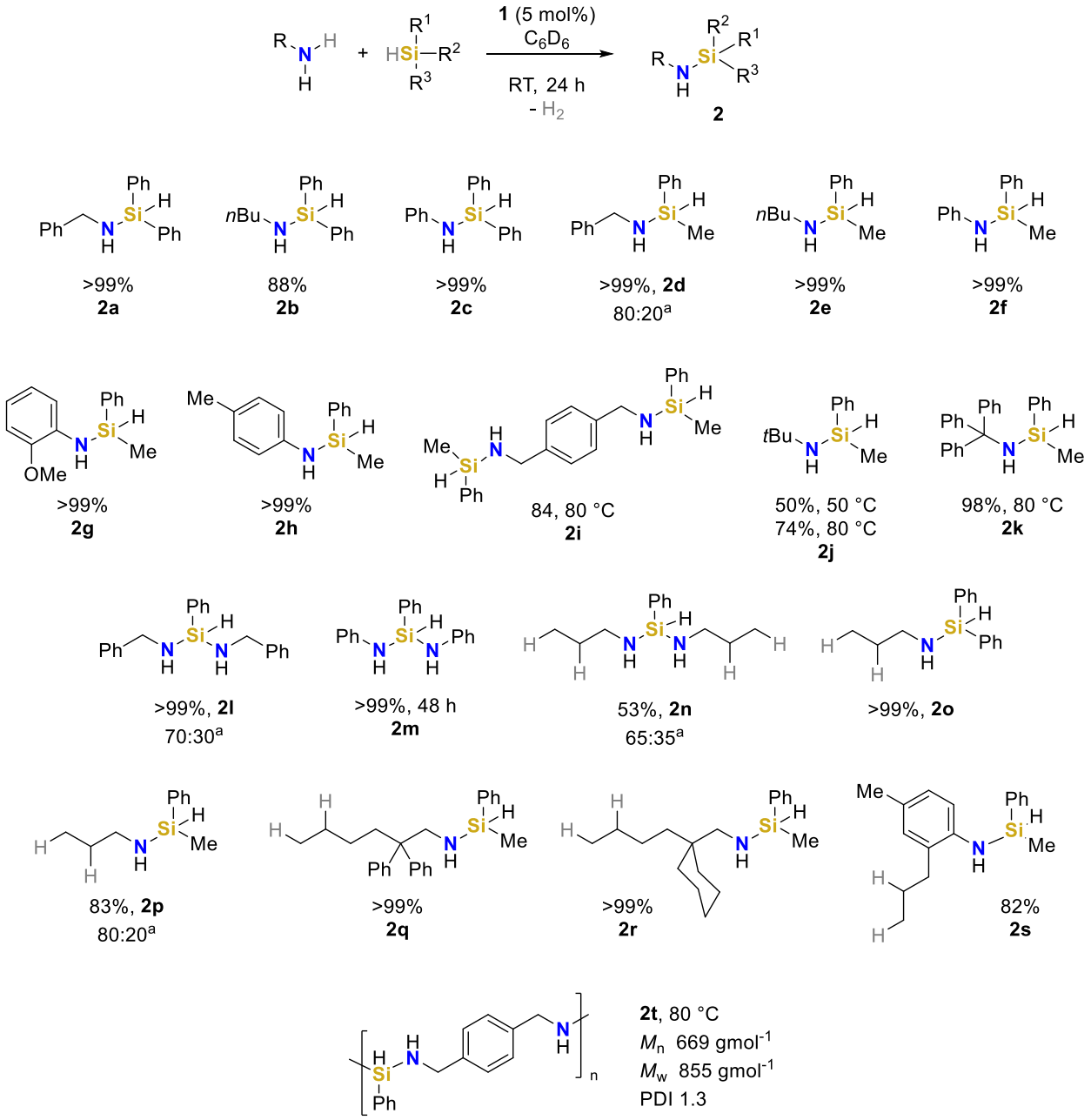
silylethers (Scheme 1). Only during the preparation of this manuscript have these classes of transformations been reported using an iron catalyst.[63]



Scheme 1. The work presented includes a wide substrate scope with over 50 examples of amino- and phosphinosilanes and silyl ethers being presented, along with mechanistic studies.

Results and Discussion

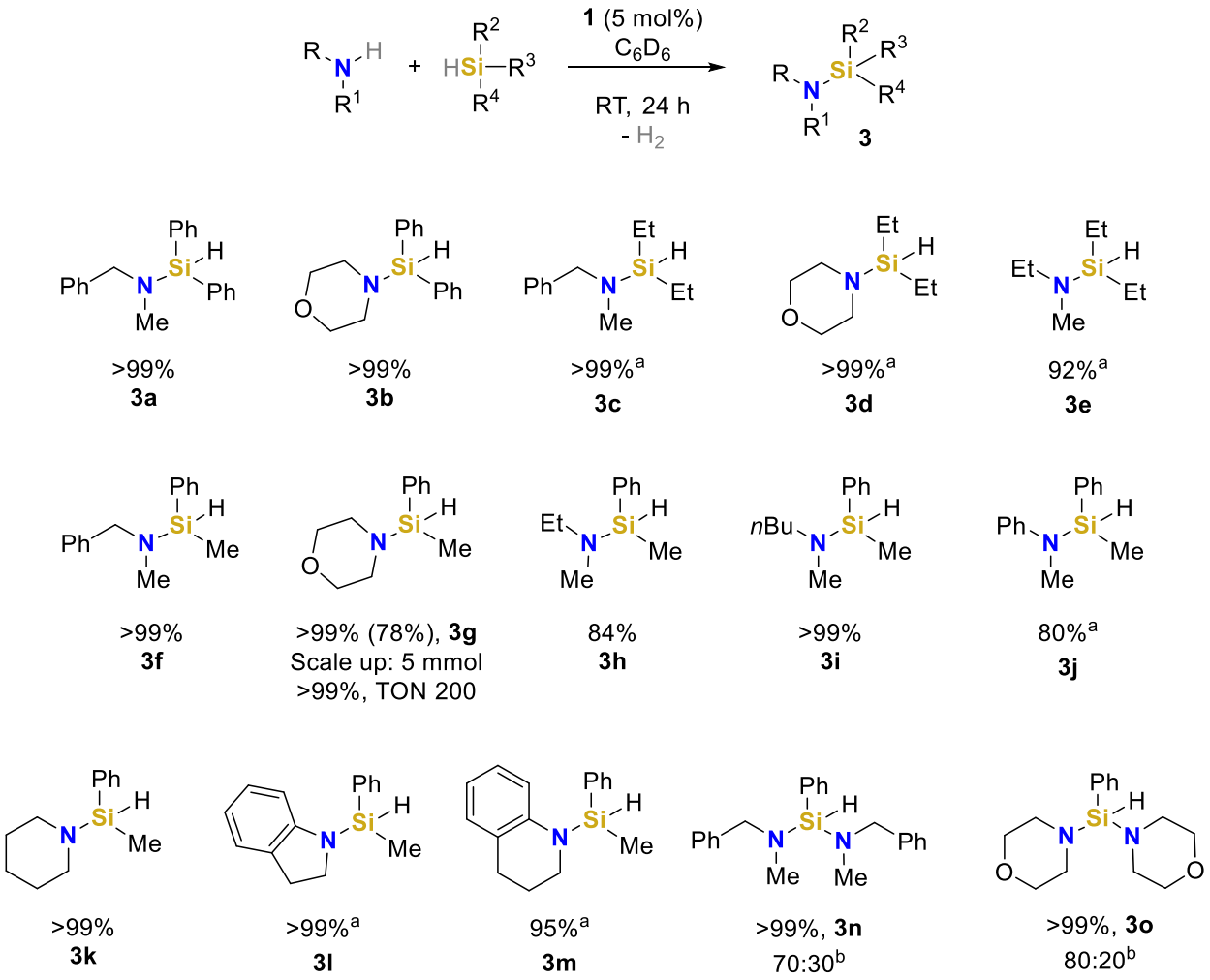
2.1 Aminosilane substrate scope



Scheme 2. Varying the primary amine. [a] mono : di.

A range of different primary amines undergo dehydrocoupling with secondary silanes at room temperature (Scheme 2). The reaction tolerates alkyl and aryl amines and works well with diphenyl- and methylphenyl silanes (**2a** to **2k**). Sterically hindered amines can be used, for example *o*-methoxyanisole gives quantitative yield of **2g** while *tert*-butylamine and tritylamine,

although requiring heating to 80 °C, do give excellent yield of product (**2j** and **2k**). Methylphenylsilane is completely consumed, quantitatively forming the disilylated product of 1,4-xylylenediamine (**2i**), while phenylsilane undergoes double amination with aniline (**2m**) in contrast benzylamine, which gives a 70:30 mixture of dimer to monomer (**2l**). No reaction is observed with tertiary silanes such as triphenylsilane and dimethylphenylsilane in conjunction with aniline or morpholine. Interestingly, substrates that contain a double bond also undergo alkene reduction (**2n** to **2s**), which we presume is a consequence of transfer hydrogenation (TH) analogous to our previous report of TH with amines and boranes.[62] We were also able to furnish oligo(silazane) **2t** as an oil. GPC analysis of this species gives a modest M_w of 855 $gmol^{-1}$. Unfortunately attempts to increase the molecular weight of the polymer, by using very forcing conditions synonymous with condensation polymerization, or dilute conditions associated with step-growth polymerization, did not increase the chain length. Reducing the catalyst loading to 1 mol% and increasing the reaction temperature to 80 °C only led to a modest increase in chain length.[64]



Scheme 3. Varying the secondary amine. [a]10 mol% **1**, 80 °C, 48 h; [b]di (shown) : mono by $^{29}Si\{^{1}H\}$ NMR, 50 °C.

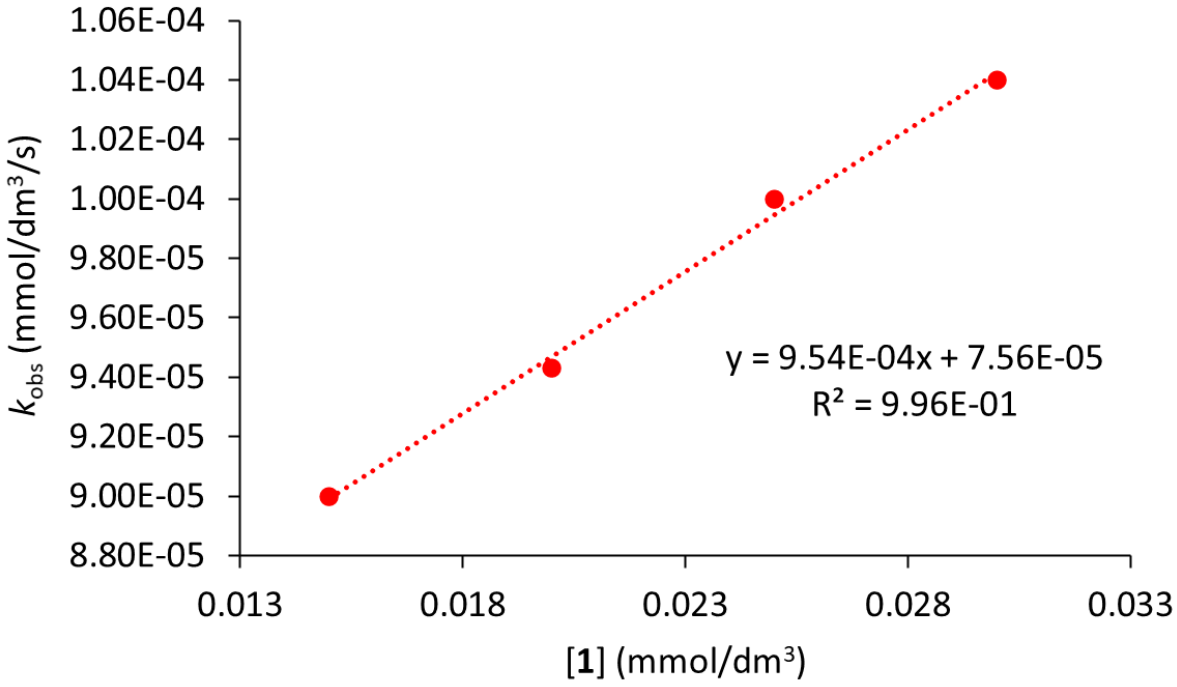
N-Methylbenzylamine and morpholine undergo dehydrocoupling with diphenyl-, diethyl- and methylphenyl silane equally well under our standard reaction conditions, giving quantitative yield of product within 24 h (**3a** to **3d**, **3f** and **3g**, Scheme 3). To demonstrate scalability 5 mmol of morpholine and methylphenylsilane with 2 mol% **1** went to completion after 48h (73% isolated yield). To demonstrate both robustness and scalability, we carried out a standard reaction of morpholine and methylphenylsilane, and after 24 h further portions of amine and silane were added via syringe. This iterative addition process was repeated until 5 mmol of each reagent was added

over the course of 10 days: the catalyst is clearly still active in solution at this time giving complete conversion to **3g** with only 5 mol% **1** after 10 days. Quantitative yield is obtained when *N*-methylbutylamine is coupled to methylphenylsilane (**3i**). Heterocyclic amines piperidine, indoline and tetrahydroquinoline give quantitative yield of the methylphenylsilyl adducts (**3k** to **3m**). Phenylsilane undergoes double amination with both methylbenzylamine and morpholine (**3n** and **3o**).

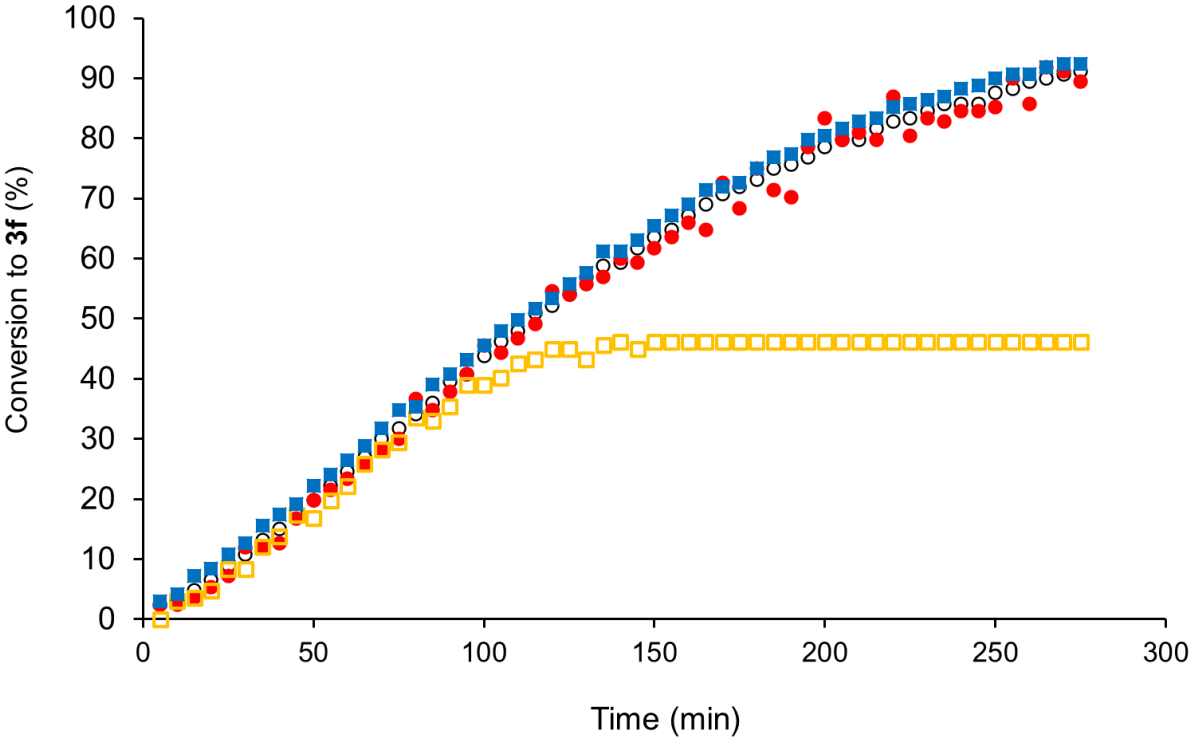
2.2 Aminosilane mechanistic investigations

Intrigued by whether our catalyst would show any similarities to other detailed amine-silane dehydrocoupling kinetics studies (for example Sarazin and Sadow both report $v = k$ [amine]^0[silane][catalyst] (Ba and Mg respectively[8, 16]) whereas Hill reports $v = k$ [amine][silane]^0[catalyst] with Mg/Ca and $v = k$ [amine][silane][catalyst]^2 with Ba[6]), we proceeded to undertake *in situ* NMR monitoring studies. We opted to use the reaction of $MeBnNH_2$ with $MePhSiH_2$. Important to note is that the reaction using 3 mol% **1** is 92% complete after around 5 hours at room temperature. Clearly the reaction is facile and, although all amine-silane dehydrocoupling reactions were allowed to react for 24 h, very high levels of conversion (>90%) can be achieved within a few hours, but extended reaction times are needed to achieve quantitative (>99%) conversion to product in most cases (Schemes 2 and 3). The data obtained suggest that the reaction has a first order dependence on the Fe-center when using **1** as reaction pre-catalyst (Figure 1a). We then studied the transformation by varying the concentration of silane. As can be seen, the reaction is independent of silane concentration (Figure 1b). As expected, with 0.5 equivalents of silane around 50% yield of product is obtained (yellow squares). In contrast, a doubling of amine loading results in an approximate doubling of the reaction rate (Figure 1c) and so a first order dependence in amine is observed.

a)


1.06E-04
1.04E-04
1.02E-04
1.00E-04
9.80E-05
9.60E-05
9.40E-05
9.20E-05
9.00E-05
8.80E-05
k_{obs} (mmol/dm³/s)
y = 9.54E-04x + 7.56E-05
R² = 9.96E-01
0.013
0.018
0.023
0.028
0.033
[**1**] (mmol/dm³)

b)


100
90
80
70
60
50
40
30
20
10
0
Conversion to **3f** (%)
0
50
100
150
200
250
300
Time (min)

c)

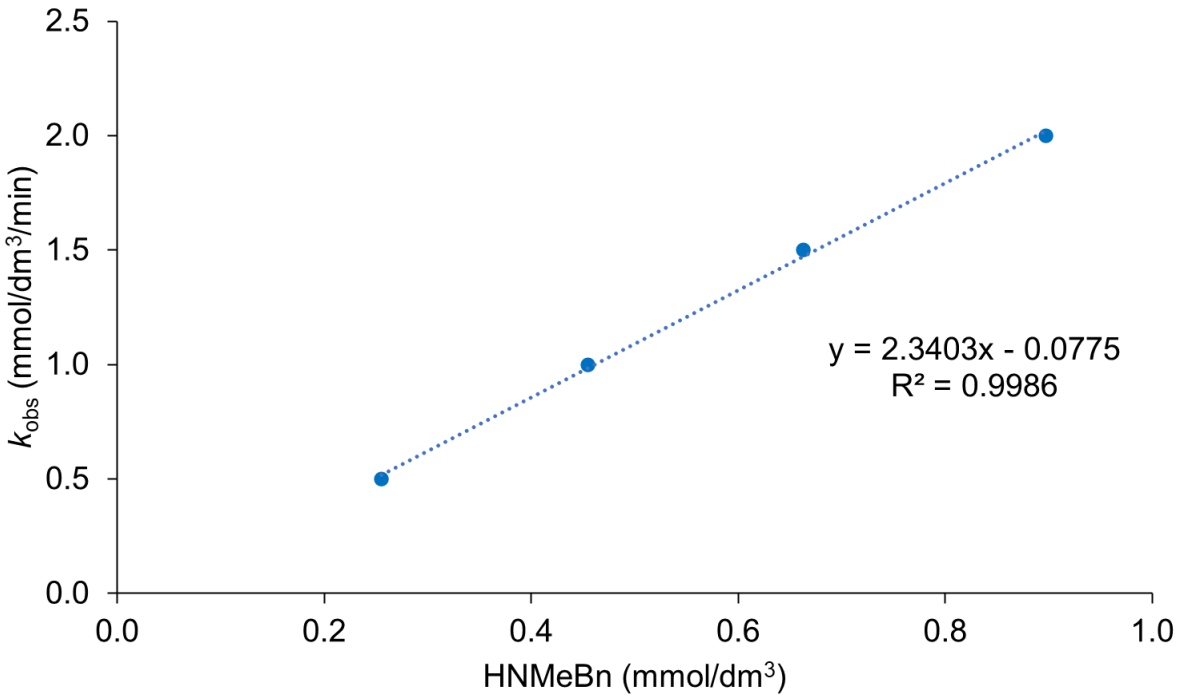


Figure 1. a) Plot showing first order relationship for formation of **3f** at different pre-catalyst loadings (6 mol%, 5 mol%, 4 mol%, 3 mol%). Conditions: 0.5 mmol silane, 0.5 mmol amine, 0.5 mL C_6D_6, RT. b) Reaction profiles showing the formation of MePhSi–NMeBn, **3f**, at different silane loadings (○ 2 equiv., ● 1.5 equiv., ■ 1 equiv., □ 0.5 equiv.) Conditions: 3 mol% **1**, 0.5 mmol amine, 0.5 mL C_6D_6, RT. c) Plot showing first order relationship for formation of **3f** at different amine loadings (2 equiv., 1.5 equiv., 1 equiv., 0.5 equiv.). Conditions: 3 mol% **1**, 0.5 mmol silane, 0.5 mL C_6D_6, RT.

Monitoring the paramagnetic region of a ^{1}H NMR spectrum for a catalytic reaction shows that iron amido complex **4** is observed throughout. Interestingly, **1** is also observed throughout the reaction. Starting from **1**, using an analogous method to that reported by Holland,[65] **4** was prepared and isolated. Use of **4** in catalysis shows that the lengthy kinetic induction period that is observed with **1** is circumvented and 92% conversion to product is obtained after 4 h, compared to 7 h when using **1** (there is 50% conversion after 90 minutes using **4** and 50% conversion after 150 minutes with **1**). This also suggests that **4** is likely to be an on-cycle species in catalysis. The reaction is first order in **4**, which we attribute to this species only contributing one Fe-center to the key

intermediate (**5**/**5'** *vide infra*).[64] Holland and co-workers have shown previously that in both the solid state and in solution iron hydride species with a methyl backbone β-diketiminate ancillary ligand exists as the dimeric hydride complex **5**.[66] At 298 K this dimeric species is observed by ^{1}H NMR in our reaction.[67] Preparation, isolation and kinetics studies with **5** give a first order fit.[64] This was unexpected, but similar results have been reported by Holland when investigating B–C bond cleavage mediated by **5**.[68] This first order fit is attributed to the presence of the open isomer (see **5'**, Scheme 4), which is in rapid equilibrium with **5**. If the amine and the iron hydride dimer (**5**) are involved in the rate-limiting step with *only one Fe–H bond* being broken during this step then only one equivalent of amine should react and therefore we would expect a first order dependence in HNMeBn when **5** is employed directly in catalysis, which is the case.[64] We therefore postulate that the rate limiting transition state involves the formation of a cyclic species, possibly of the form **5'**$_{TS}$, followed by release of hydrogen gas and formation of **4** and **5**. Collapse of **5'**$_{TS}$ might proceed via a mixed hydride-amido dimer such as **6**. We have evidence for the ability for such species to form; reacting **5** with H_2N^nBu and $MePhSiH_2$ **6** is immediately observed by ^{1}H NMR and X-ray quality crystals were readily obtained (Figure 2).

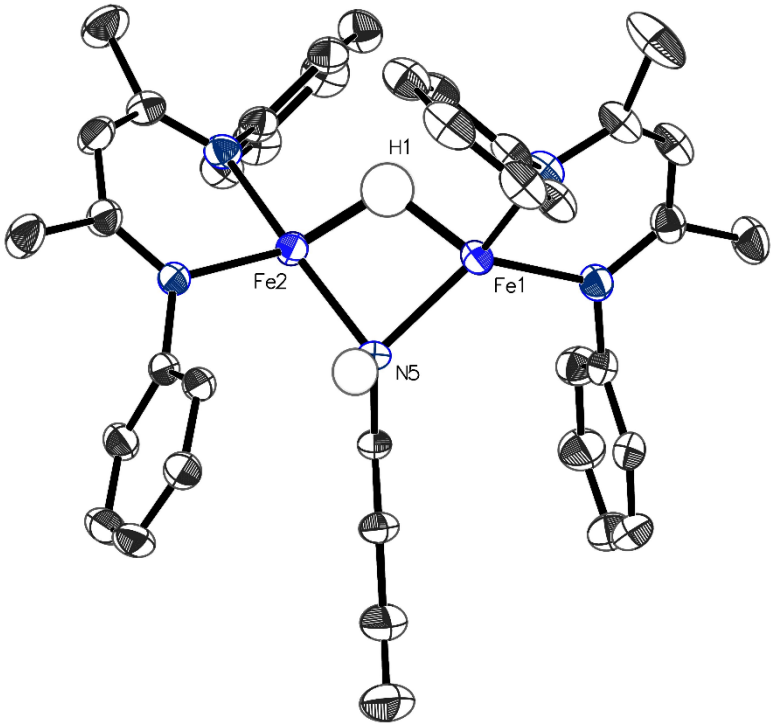
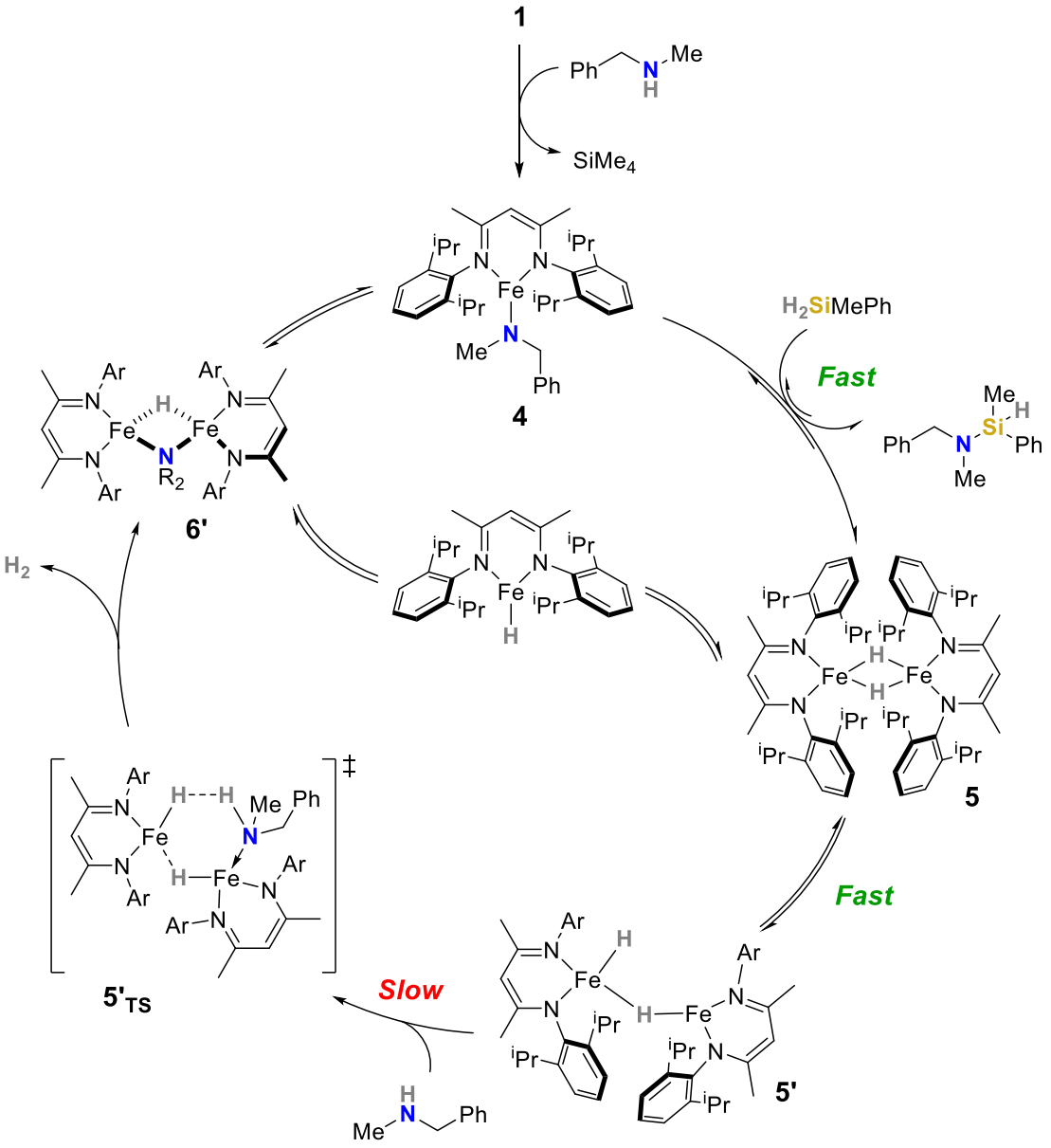


Figure 2. Mixed hydride-amido dimer (**6**) isolated from reaction of $^{n}BuNH_2$, $PhMeSiH_2$ and **5**.[64] Ellipsoids are represented at 50%. Except for the hydride ligand and N-H, all hydrogen atoms, solvent, disorder and the 2,6-diisopropyl groups have been omitted for clarity.

In order to probe the nuclearity of the species present in solution, DOSY experiments were performed[69] on a mixture of **5** and $^{n}BuNH_2$ in C_6D_6; disappearance of **5** is observed with H_2 release and formation of dimers ($D = 5.04\text{-}5.48 \times 10^{-10}$ m^2 s^{-1}), primarily consisting of complex **6** but formation of other mixed dimeric species cannot be ruled out ($r_{solution} = 8.2$ Å).[70] Pleasingly when reacting pre-catalyst **1** with a mixture of amine ($^{n}BuNH_2$) and $PhMeSiH_2$ in C_6D_6 multiple species were observed; the slower peaks were analyzed and showed similar diffusion coefficients ($D = 4.50\text{-}5.95 \times 10^{-10}$ m^2 s^{-1}) to the experiment above and a large solution hydrodynamic radius ($r_{solution} = 8.5$ Å) synonymous with dimers. These results are in line with the appearance of dimer **5** during

kinetic ^{1}H NMR analysis and the order in **5** which suggests it exists as an active dimer throughout catalysis. Furthermore, calculation of the hydrodynamic radius of **6** using single crystal data[71] is very similar to the solution data obtained (r_{solid} = 9.2 Å)

Combined, these data have allowed us to postulate a preliminary catalytic cycle (Scheme 4). The steps in the catalytic cycle are in-line with reports from Sadow,[16] Sarazin[8] and Hill[6] in that catalyst activation forms an initial metal-amido species which then undergoes metal-hydride formation and release of the aminosilane product. Unlike the report from Sarazin, where hydride transfer is rate limiting, or Sadow where attack of silane by an Mg-amido species is rate limiting, the subsequent proton transfer between *N*-methylbenzylamine and iron-hydride is probably the slow step in our reaction.



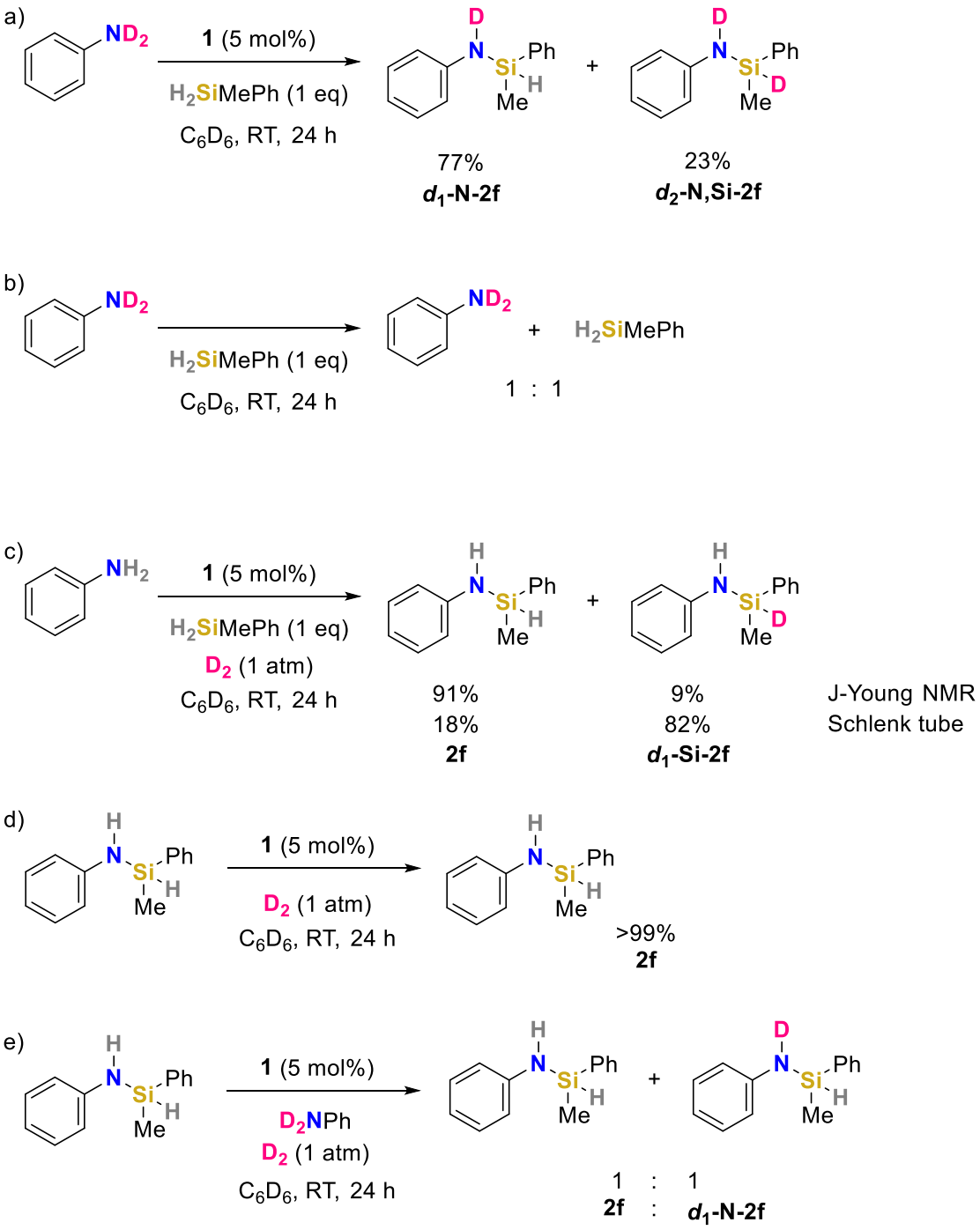
Scheme 4. Postulated mechanism based on NMR studies.

Deuterium labelling using d_2-aniline as an easily accessible substrate gives a primary KIE for the formation of **2f** of 2.42(3),[64] which may indicate proton transfer is occurring through a non-linear transition state. This also supports our proposed catalytic cycle where the reaction is first order in amine. We have also undertaken Arrhenius and Eyring analysis of catalysis mediated by **1**: Ea = 54.59 kJ mol^{-1} ± 0.03; $\Delta H^{\ddagger}$ = 12.43 kcal mol^{-1} ± 0.02; $\Delta S^{\ddagger}$ = -5.13 cal mol^{-1} K^{-1} ± 0.01;

$\Delta G^{\ddagger}$ = 13.95 kcal mol^{-1} ± 0.2. This is in line with reports using Mg[6] (13.9 kcal mol^{-1}) and Ba[8] (15.6 kcal mol^{-1}) systems. The latter study from Sarazin also reports similar Ea and $\Delta G^{\ddagger}$ to our system. The importance of $\Delta H^{\ddagger}$ to the activation energy barrier for our process is highlighted by the primary KIE value. We can rationalize the low $\Delta S^{\ddagger}$ obtained by looking at the process of **5**/**5'** and thus onward formation of **5'**$_{TS}$. In these steps an Fe–H bond is broken and H–H bond begins to form. Akin to work from Holland on the likelihood of **5'** to be a reaction intermediate, this 'interchange mechanism' is often linked to very low $\Delta S^{\ddagger}$.[67]

On closer inspection of the deuterium labelling study we can report another intriguing result. Reaction of d_2-aniline with methylphenylsilane gives a mixture of PhDN–SiHMePh (***d*$_1$-2f**) and PhDN–SiDMePh (***d*$_2$-2f**) in a 77:23 ratio (Scheme 5a). In the absence of catalyst there is no H/D exchange and no dehydrocoupling (to give product(s) of the form **2f**, Scheme 5b). To determine whether the HD released from reaction of d_2-aniline with methylphenylsilane is responsible for silane deuteration, presumably due to HD activation by iron catalyst, we performed the standard reaction under an atmosphere of D_2 (Scheme 5c). Reaction in a J-Young NMR tube gives a small amount of Si–D product (***d*$_1$-Si-2f**), but no deuterium incorporation at nitrogen takes place (in the aniline starting material or aminosilane product). A standard reaction, of the form presented in Scheme 5a, will generate an estimated 6 bar of H_2/HD/D_2 pressure in a J-Young NMR tube (based on the Ideal Gas Law), whereas the reactions in Scheme 5c are back-pressurized with 1 bar D_2, hence the difference in J-Young NMR tube deuterium incorporation results. The same reaction in a Schlenk tube with a large headspace back-filled with 1 atm. D_2 gives 82% ***d*$_1$-Si-2f**. These data indicate that a greater number of equivalents of D_2 leads to more D-incorporation: the same reaction under a D_2 atmosphere was performed in the same scale in a sealed Schlenk (25 mL) without stirring and it showed 87% deuterium incorporation, suggesting that mass transfer is not

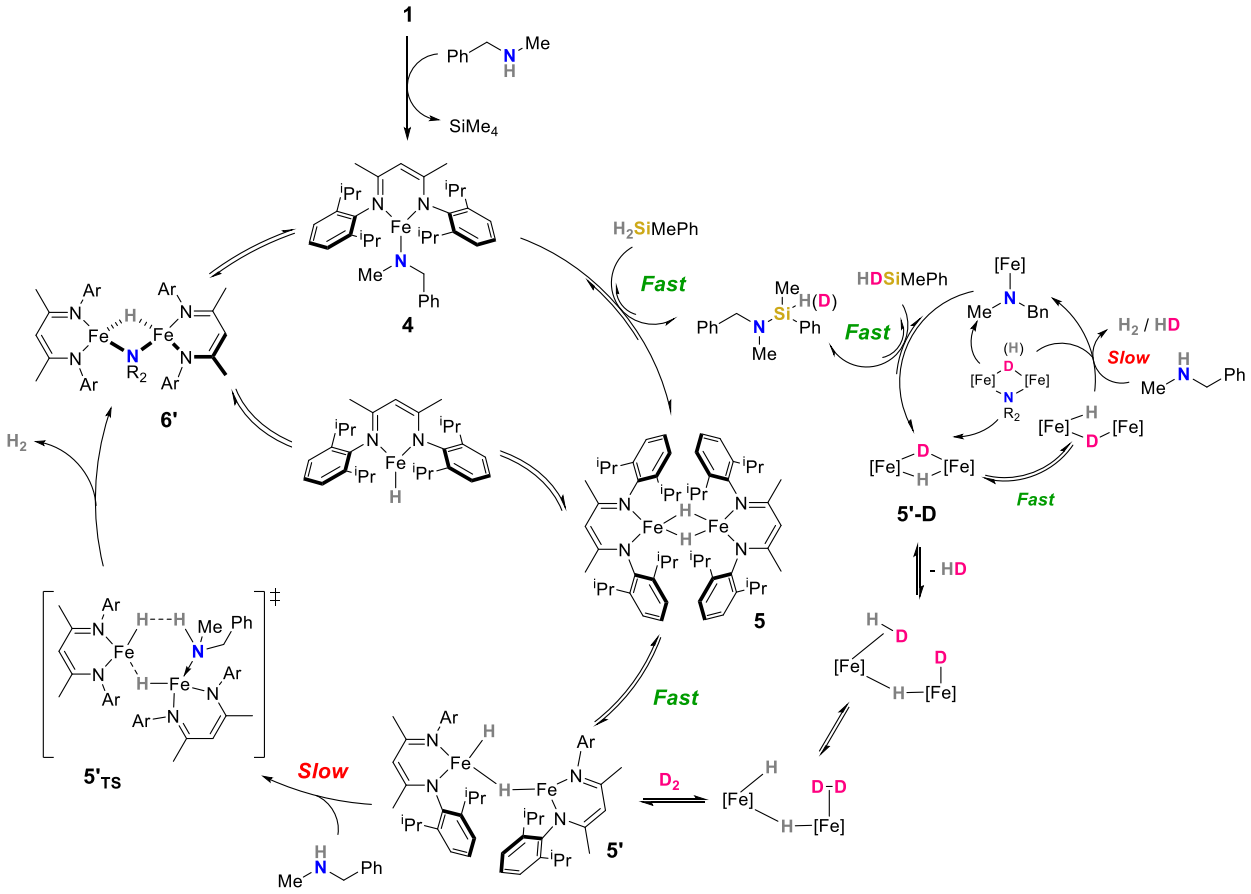
influencing the reaction outcome. N–H bond activation is likely more challenging than other steps in the catalytic cycle; in-keeping with our postulated catalytic cycle. **2f** does not show any deuteration when exposed to 1 atm. D_2 (Scheme 5d): the iron catalyst is not able to further functionalize **2f**. Repeating this reaction of **2f** in the presence of one equivalent of d_2-aniline, 1 atm. D_2 and 5 mol% **1** gives a 1:1 mixture of **2f** and ***d*$_1$-N-2f**, therefore indicating that N-Si bond formation is reversible (Scheme 5e). Furthermore H/D exchange is not observed when **2f** is mixed with d_2-aniline. Si–H bond deuteration is not observed under these conditions indicating that silazane formation is fast and reversible, precluding any deuteration of free silane released in the reverse reaction. This also suggests that silane deuteration occurs via a different catalytic cycle. Taking **1**, H_2NPh (to allow catalyst activation) and methylphenylsilane under an atmosphere of D_2 does not show deuterium-incorporation at nitrogen, indicating that direct formation of iron(II)-deuteride from iron(II)-amido does not take place. Reaction of methylphenylsilane, D_2 and **1** (5 mol%) gives 9% MePhSiHD further indicating that H/D exchange via Si–H activation is feasible in the presence of **1** and this process is currently under investigation.



Scheme 5. Studies into deuterium incorporation into **2f**.

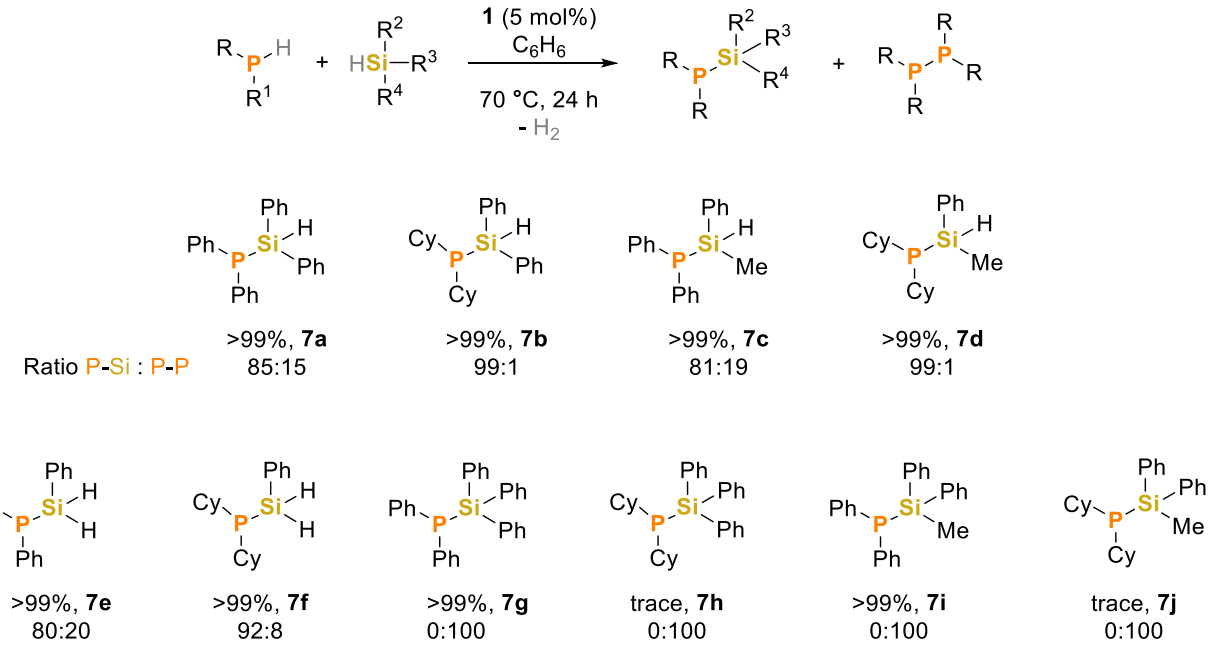
Based on the combined experimental and literature data an updated catalytic cycle for reaction of $PhNH_2$ with $MePhSiH_2$ in the presence of D_2 and incorporating H/D exchange can be proposed

(Scheme 6). The open-isomer was invoked as possible mechanistic scenario for hydride ligand exchange with D_2 from **5** to **5'-D** by Holland and co-workers.[65] The catalytic cycle for Si–D bond formation could then proceed in a similar manner to that of Si-N bond formation, in that there is a fast reversible equilibrium between **5'-D** and the open isomer, reaction with amine releases H_2 or HD and forms **4**, it would be at this point that fast reversible equilibrium between silane and **5'-D** allows deuteration of the silane.



Scheme 6. Revised catalyst cycle for dehydrocoupling demonstrating that, starting from a common intermediate (**5'**) a second cycle that could account for Si–D bond formation due to H/D exchange in the presence of D_2.

2.3 Phosphinosilane substrate scope



Scheme 7. Scope of phosphinosilane reactivity.

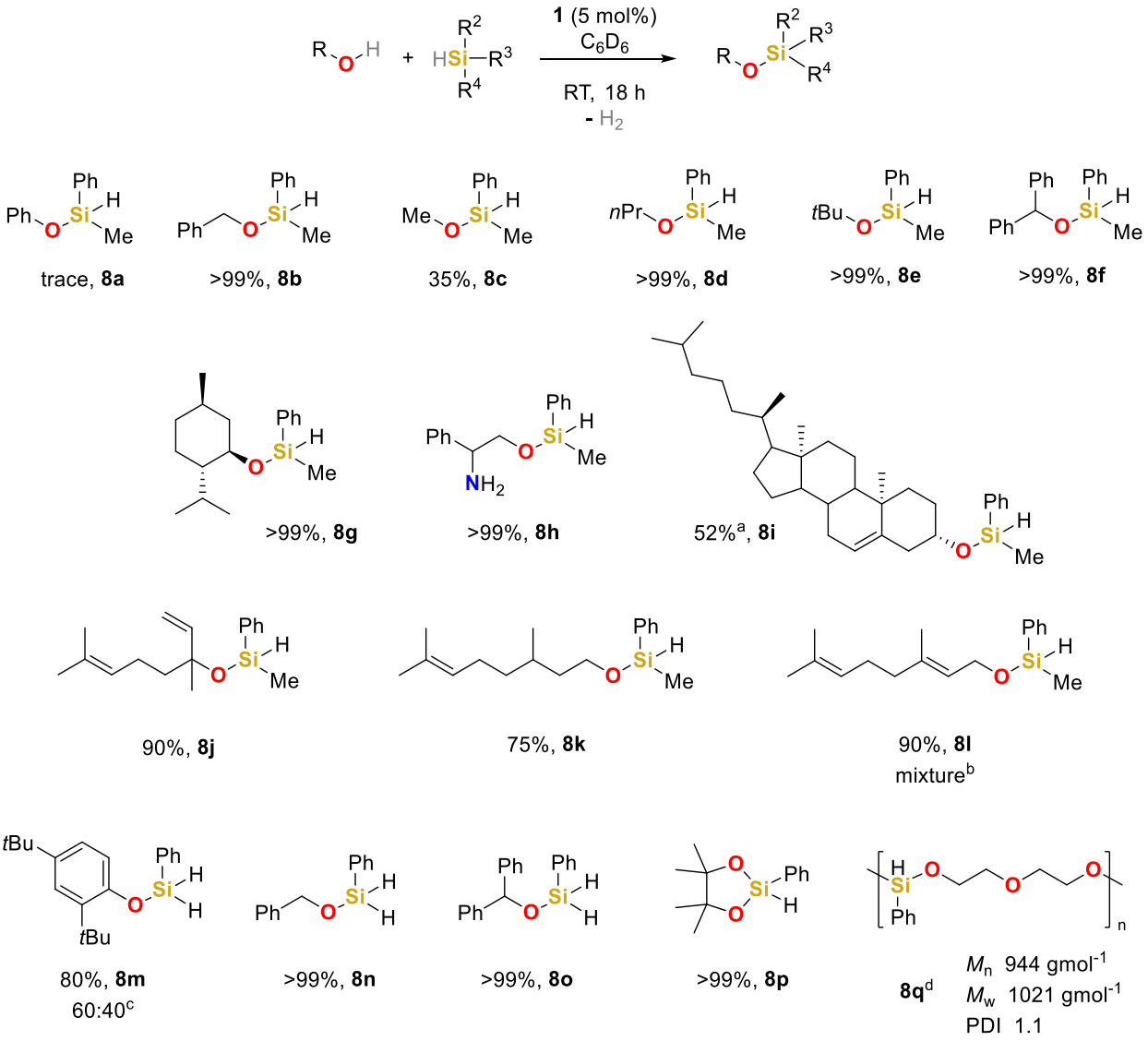
Given the reaction scope achieved with amines, we expected to achieve good reactivity with phosphines. When we began our optimization studies it was immediately clear that phosphine-silane dehydrocoupling is a more challenging target for pre-catalyst **1**: in order to obtain high conversion to the dehydrocoupled product heating to 70 °C is necessary (Scheme 7). For comparison Waterman has heated to 90 °C and Manners to 100 °C with their Zr[22] and BCF[20] catalyzed processes. Also apparent in our catalysis is the potential for competitive phosphine homodehydrocoupling to take place; this is not unexpected as we have previously reported diphosphane synthesis via dehydrocoupling using comparable reaction conditions.[57] Homodehydrocoupling becomes competitive with the desired heterodehydrocoupling reaction when tertiary silanes (triphenyl- and methyldiphenyl-) are employed (**7g** to **7j**) and in the case of diphenylphosphine, complete conversion to tetraphenyldiphosphane ($Ph_2P–PPh_2$) is observed (**7g** and **7i**). When dicyclohexylphosphine is reacted with tertiary silanes, although the transformation is completely selective for homodehydrocoupling, only trace amount of product is observed. This

is in-line with our previous report on phosphine dehydrocoupling i.e. we do not believe that the silane plays an active role in assisting homodehydrocoupling. Moreover, under the catalytic reaction conditions, homodehydrocoupled product $(Ph_2P)_2$ does not react with Ph_2SiH_2 even after 3 days at 80 °C: our system does not proceed via activation of the P–P bond (as achieved by Manners[20] and Stephan[24]) but rather through activation of the P–H bond. In contrast, when secondary silanes are employed, dicyclohexylphosphine gives much better selectivity for the desired heterodehydrocoupled product. 99:1 Hetero:homodehydrocoupled product is obtained with dicyclohexylphosphine with both diphenylsilane and methylphenyl silane (**7b** and **7d**), whereas this ratio drops to 85:15 and 81:19 respectively when $HPPh_2$ is employed (**7a** and **7c**). Again, this is a direct reflection of the ease with which the phosphines homodehydrocouple. Similar to Harrod's report using titanocenes, phenylsilane only reacts once with $HPPh_2$ and $HPCy_2$ yielding $R_2PSiPhH_2$ selectively.

2.4 Silylether substrate scope

The inherent oxophilicity of Fe(II) does not appear to be limiting when alcohols are employed as coupling partners. However, the nature of the alcohol appears to be important and there is an interesting divergence in reactivity whereby phenol only gives a trace amount of product (**8a**, Scheme 8) whereas aliphatic alcohols give almost quantitative yield of siloxane (**8b** to **8g**, with the exception of methanol which only gives 35% **8c**). If the silane is changed from methylphenylsilane to phenylsilane then good levels of mono-silylated phenolic product is achieved (**8m**). Returning to focus on reactivity achieved with methylphenylsilane, 2-phenylglycinol shows interesting selectivity with the alcohol reacting preferentially (**8h**). Elaborate organic motifs can undergo heterodehydrocoupling to generate the silylated product including (−)-menthol (**8g**), cholesterol

(**8i**), linalool (**8j**), β-citronellol (**8k**) with no evidence for double bond functionalization of isomerization. Phenylsilane reacts with benzylalcohol and benzhydrol quantitatively (**8n** and **8o**) and with pinacol alcohol to give the dioxasilolane (**8p**). Oligosiloxane, **8q**, derived from phenylsilane and diethylene glycol was also prepared as a solid with very narrow PDI and *DP* of 4.5. DSC shows two T_m peaks (245.7 °C and 256.2 °C) which may indicate the presence of both linear and cyclic oligomers.



Scheme 8. A range of alcohols can be protected as silylethers using our heterodehydrocoupling methodology. [a]71% achieved after 24 h at 50 °C; [b]intractable mixture of mono- and di-substituted silane and also likely to contain functionalization/isomerization of double bond(s); [c]mono:di; [d]80 °C, 24 h.

3. Conclusions

In summary, we have presented a detailed study into the reactivity of a simple iron pre-catalyst **1** towards silane heterodehydrocoupling. Amines react well with secondary silanes, which is complementary to the state-of-the-art in the literature, and give good selectivity for mono-substituted product. A detailed mechanistic study was undertaken which showed that the rate-limiting step was likely to be protonolysis of an iron hydride dimer to release hydrogen and generate an iron-amido. We believe we have provided strong evidence for the presence of iron dimers being active on-cycle species during catalysis. Deuterium labelling studies show a modest primary KIE that support rate limiting protonolysis and suggest that the RLS proceeds via a non-linear transition state. Unexpectedly, Si–D formation in the presence of D_2 appears to be more favorable than N–D formation. However, this is in-line with kinetics results. Finally, we have shown that phosphinosilane formation is possible under mild conditions, while we have also generated a diverse range of structurally complex silylethers: valuable building blocks in organic synthesis.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Analysis data and NMR spectra for all products (PDF). CCDC 1978051 contains the

supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/structures

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